

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Process for the Production of Bisphenols

We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of bisphenols. More particularly, this invention relates to a process for the production of bisphenols by reacting a phenol with a ketone in a reaction medium containing an insoluble resin having at least one mercapto group chemically bonded thereto and also containing a second resin which is a solid, insoluble, ion-exchange resin having pendant sulfonic acid groups.

The production of bisphenols has been accomplished in the past, by reacting a phenol with a ketone in a reaction medium containing a mineral acid such as hydrochloric acid, or sulfuric acid. This method of producing bisphenols, however, has been found to present serious problems, especially from a commercial standpoint. Mineral acids being highly corrosive, attack and corrode the apparatus in which the reaction is being conducted. Also, since mineral acids are soluble in phenols and ketones, it is extremely difficult to remove mineral acids from the unreacted starting materials. In addition, the catalytic activity of mineral acids decreases markedly in the presence of water, formed during the reaction, until a concentration of about 1.2 percent by weight water, based on the weight of the starting reactants when the molar ratio of reactants used as one mole ketone to 10 moles of a phenol and the amount of mineral acid used

is one percent by weight, mineral acids exhibit little, if any, catalytic activity.

In an attempt to enhance the catalytic activity of mineral acids, it has been proposed to utilize as a promoter therewith, a mercaptan such as ethyl mercaptan. This expedient has not proved to be particularly effective for the purpose of providing a suitable catalyst system. The catalyst system still remains corrosive to the apparatus in which the reaction is being conducted and further, still presents serious processing problems with respect to removal and recovery of mercaptan, unreacted phenol and unreacted ketone from the mineral acids.

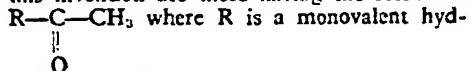
The use of mercaptan, as described, also presents a problem in that, in some form, it remains in the bisphenol product and causes an undesirable odor and/or contaminates the bisphenol product with sulfur.

The present invention provides for the production of bisphenols by reacting a phenol with a ketone in a reaction system containing an insoluble resin (insoluble in the reaction mixture) having at least one mercapto group chemically bonded thereto and also containing a second resin which is a solid, insoluble (insoluble in the reaction mixture) ion-exchange resin having pendant sulfonic acid groups.

By utilizing a catalyst system of an insoluble mercapto-resin as defined in conjunction with a solid-insoluble ion-exchange resin containing pendant sulfonic acid groups, the rate of reaction between the phenol and the ketone is significantly increased, higher conversions of ketone are effected, up to 100 percent, and the bisphenol produced is substantially free of undesirable by-products such as Dianins Compound and sulfur. Also, it is now possible to effect these advantages in a reaction medium containing an excess of say 1.2 percent by weight water, under

conditions of reaction as previously specified with respect to mineral acids. Furthermore, there is no odor problem with respect to the catalyst system of this invention.

- 5 Among ketones, suitable for purposes of this invention are those having the formula:

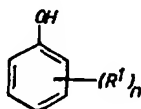


- 10 rocarbon radical generally containing a maximum of 12 carbon atoms and preferably containing a maximum of six carbon atoms.

- 15 Illustrative of suitable ketones falling within the scope of the formula noted are the following: saturated aliphatic ketones such as dimethyl ketone, chloroacetone, methyl ethyl ketone, methyl *n*-propyl ketone and methyl isobutyl ketone; aromatic ketones such as phenyl methyl ketone; unsaturated ketones such as mesityl oxide.

- 20 Other suitable ketones include cyclohexanone, 2-methyl cyclohexanone, 3-methyl cyclohexanone and 4-methyl cyclohexanone; polyketones such as acetonyl ketone.

- 25 Phenols which can be reacted with the ketones to produce bisphenols, in accordance with this invention are the broad class of phenolic compounds which have at least one position other than meta position unsubstituted, as for example, those having the formula:



- 35 wherein each individual R¹ which can be the same or different is an alkyl radical such as methyl, ethyl *n*-propyl, or *n*-hexyl, preferably an alkyl radical having one to four carbon atoms inclusive, or a halogen atom, i.e., chlorine, bromine, iodine or fluorine, or an alkoxy radical such as methoxy, ethoxy, *n*-propoxy or *n*-amyloxy, preferably an alkoxy radical having one to four carbon atoms inclusive, or an aryl radical such as phenyl or a cycloaliphatic radical such as cyclohexyl; *n* is an integer having a value of zero to four inclusive with the further limitation
- 40 that at least one position other than meta is unsubstituted.

- 45 Suitable phenols, include among other, phenol, the cresols, *m*-ethyl phenyl *m*-*n*-propyl phenol, *m*-isopropyl phenol, *m*-*n*-butyl phenol, *m*-sec-butyl phenol, *p*-tert-butyl phenol, *o*-methoxy phenol, *m*-ethoxy phenol, *p*-*n*-propoxy phenol, *m*-amyloxy phenol, *m*-chloro phenol, *m*-bromo phenol, *p*-chloro phenol, 2,6-dimethylphenol, 2-methyl-6-methoxy phenol, 2-methyl-4-chloro phenol
- 50 and *o*-phenyl phenyl.
- 55

Ion-exchange resins which are suitable for this invention are solid, insoluble resins made up of polymeric skeletons with pendant sulfonic acid groups chemically bonded thereto.

60 The exchange potential of the chemically bonded sulfonic acid groups and the number of such groups available for contact with the reactants indicates the catalytic effectiveness of a particular ion-exchange resin. Thus, although the number of sulfonic acid groups chemically bonded to the polymeric skeleton of the resin determines the theoretical "exchange capacity" thereof, a more accurate criterion of catalytic effectiveness is the number of sulfonic acid groups which are in fact available for contact with the reactants. This contact can occur on both the interior and exterior surfaces of the ion-exchange resin. As a general rule, therefore, a form of ion-exchange resin which provides a maximum amount of surface area, e.g., porous microspheres or beads is highly desirable.

In general, the greater the "exchange capacity" of an ion-exchange resin, i.e., the greater the number of milliequivalents of acid per gram of dry resin, the more desirable the resin for purposes of this invention. Resins having an "exchange capacity" greater than about two milliequivalents of acid per gram of dry resin are preferred. Among the ion-exchange resins which are highly desirable are: sulfonated styrene-divinylbenzene resin, sulfonated cross-linked styrene resins, phenol-formaldehyde-sulfonic acid resins and benzene-formaldehyde-sulfonic acid resins. These and other such resins are available commercially under the trade names such as: Amberlite XE-100 (a Registered Trade Mark of Rohm and Haas Co.); Dowex 50-X-4 (a Registered Trade Mark of Dow Chemical Co.); Permutit QH (a Registered Trade Mark of Permutit Co.); and Chempro C-20 (a Registered Trade Mark of Chemical Process Co.).

Particularly preferred for purposes of this invention are ion-exchange resins, as described, which are substantially water-free, that is, ion-exchange resins containing less than about one percent by weight of water. Ion-exchange resins can be rendered substantially water-free in a manner as described in U.S. patent 3,221,061.

Among suitable insoluble resins having at least one mercapto group chemically bonded thereto are resins obtained by polymerizing polythiiranes as described in Example 1 or by using phenolic catalysts as described in U.S. patent 2,962,457.

Other such suitable resins are obtained by chemically bonding mercapto groups to an ion-exchange resin in a manner described in U.S. patent 3,153,001 or by reacting an ion-exchange resin with sulfur. The mercapto resins promote the catalytic activity of the ion-exchange resins.

The reaction between the phenol and ketone can be conducted over a wide temperature range. As a rule the reaction is conducted at temperatures of 50° C. to 150° C. Preferred temperatures are in the range of 50° C. to 110° C.

Theoretically one mole of ketone reacts with two moles of a phenol. In practice, however, the mole ratio of reactants used varies from 3 to 1 to 20 to 1 phenol of ketone. It is preferred to use the reactants in a mole ratio of 4 to 1 to 12 to 1 phenol to ketone.

The ion-exchange resin is used in amounts sufficient to catalyze the reaction, generally in an amount of 0.4 equivalent to 1 equivalent (based on the sulfonic acid groups) per mole of ketone.

The amount of mercapto-resin used is generally 0.1 to 1 equivalent (based on the mercapto groups) per mole of ketone. Based on the amount of ion-exchange resin containing sulfonic acid groups, the amount of mercapto resin used is 1/4 to 1 equivalent per equivalent of the sulfonic acid-ion exchange resin.

The insoluble catalyst system of this invention, the two resins as previously described, are removed from the reacted mixture by filtration. The bisphenol reaction product is conveniently recovered from the reacted mixture by crystallizing the product with phenol and then mechanically separating the bisphenol.

The reaction described herein can be conducted under atmospheric, subatmospheric or superatmospheric pressures.

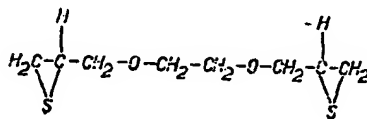
The following examples further illustrate the present invention and are not intended to limit the scope thereof in any manner.

#### EXAMPLE 1

To a mixture of 470 grams of phenol and 29.0 grams of acetone, a mole ratio of 10 to 1, there was added a catalyst system made up of 125 grams of Dowex-50-X-4 an ion-exchange resin having chemically bonded sulfonic acid groups and 40 grams of Ionac X-S an ion-exchange resin having chemically bonded mercapto groups. The mixture was heated for three hours at 70° C. yielding 74.5 grams of crude bisphenol. This represented a conversion to bisphenols of 65.4 percent based on acetone.

#### EXAMPLE 2

A. Preparation of a mercapto-polymer  
A compound of the formula:



bis(2,3-epithiopropylether) of ethylene glycol was homopolymerized by heating in methanol, for 50 minutes at a temperature of 36° C. and then for three hours at 68° C. The methanol was distilled off yielding a homopolymer containing mercapto groups.

Two 300 gram reaction mixtures, reaction mixture A and Control I, were prepared using phenol and acetone as the reactants in a mole ratio of 10 to 1.

To Control I there was then added 10 grams of Amberlite, a sulphonated styrene-divinylbenzene ion exchange resin.

To reaction mixture A there was added 10 grams of Amberlite, and two grams of the resin noted in "A" above.

Each reaction mixture was heated to 70° C. and maintained at 70° C. for two hours and 20 minutes. Each mixture was then cooled rapidly and filtered through a sintered glass funnel.

The 2,2 - bis(p - hydroxyphenyl)propane produced from Control I has an undesirable reddish tinge.

The 2,2 - bis(p - hydroxyphenyl)propane produced from reaction mixture A was free of undesirable reddish tinge.

Although the present invention has been described with reference to conducting the reaction between the phenol and ketone in the presence of both resins, it is to be understood that the reaction mixture containing the phenol and ketone can be passed through initially the resin having the mercapto groups and then passed through the ion-exchange resin having the sulfonic acid groups for reaction.

#### WHAT WE CLAIM IS:—

1. A process for preparing a bisphenol which comprises reacting a phenol with a ketone in a reaction medium containing an insoluble resin having at least one mercapto group chemically bonded thereto and containing a second resin which is a solid, insoluble ion-exchange resin having pendant sulfonic acid groups.
2. A process as claimed in claim 1 wherein the phenol is phenol.
3. A process as claimed in claim 1 or claim 2 wherein the ketone is acetone.
4. A process as claimed in any one of claims 1 to 3 wherein the said resin having at least one mercapto group per molecule is one which has been formed from bis(2,3-epithiopropylether) of ethylene glycol.
5. A process as claimed in any one of claims 1 to 4 wherein the said resin having at least one mercapto group per molecule is used in an amount of 0.1 to 1 equivalent, based on the mercapto groups, per mole of ketone.
6. A process as defined in any one of claims 1 to 5 wherein the ion-exchange resin having pendant sulfonic acid groups is used

in an amount of 0.4 equivalent to 1 equivalent, based on the sulfonic acid groups, per mole of ketone.

- 5 7. A process as claimed in any one of claims 1 to 6 wherein the amount of said resin having at least one mercapto group per molecule in the reaction mixture is from  $\frac{1}{3}$  to 1 equivalent per equivalent of the sulfonic acid ion exchange resin present, based on  
10 the mercapto groups and the sulfonic acid groups.

- 15 8. A process as claimed in any one of claims 1 to 7 in which the initial mole ratio of the phenol to the ketone is from 4 to 1 to 12 to 1.

- 20 9. A modification of the process for preparing a bisphenol as claimed in any one of claims 1 to 8 which comprises contacting a mixture of a phenol and a ketone with an insoluble resin having at least one mercapto group and thereafter reacting this mixture together in contact with a solid, insoluble ion-exchange resin having pendant sulfonic acid groups.

10. A process as claimed in any one of claims 1 to 9 in which the reaction takes place at a temperature of from 50°C. to 110°C. inclusive. 25

11. A process as claimed in claim 1 for the preparation of a bisphenol substantially as herein described with reference to either of the specific Examples. 30

12. A bisphenol whenever prepared by the process claimed in any one of claims 1 to 11. 35

13. A catalyst system suitable for use in the process claimed in claim 1 which system comprises an insoluble resin having at least one mercapto group per molecule and a second resin which is a solid, insoluble ion-exchange resin having pendant sulfonic acid groups. 40

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